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Metal Interactions at Sulfide Mineral Surfaces Part 2. Adsorption and Desorption of Lanthanum

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METAL INTERACTIONS AT SULFIDE MINERAL SURFACES:

PART II. ADSORPTION AND DESORPTION OF LANTHANUM

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ABSTRACT

Lanthanum, a representative lanthanide element, is mined like other ore minerals and can potentially be transported from tailing piles to contaminate surface or subsurface water. The role of adsorption and desorption in determining La(III) mobility warrants definition.

Batch-type adsorption experiments with four sulfide minerals -- chalcocite, galena, pyrite, and sphalerite -- were used to investigate the adsorption and desorption behavior of La(III) in the presence of ethylenediaminetetraacetic acid (EDTA), a model humic substance. Linear adsorption was found in all cases. The presence of EDTA, soluble complexing ligand, caused a 5- to 10-fold increase of La(III) adsorbed and also changed the order of adsorption of the four minerals. In the presence of EDTA, the order of La(III) adsorption is pyrite > chalcocite > galena > sphalerite; in the absence of EDTA, the order is chalcocite > pyrite > galena > sphalerite.

La(III) adsorption is pH dependent and exhibits a distinct adsorption edge, the pH_{50} being 5.3 for pyrite and 6.4 for galena. (pH_{50} is the pH at which 50 % of the initial metal concentration is adsorbed). Two factors, sulfide mineral type and metal concentration, determine the exact pH value. For pyrite, the pH_{50} for La(III) increases from 5.3 to 6.2 as the concentration changes from 6.7 to 1.2×10^{-4} M.

The La(III)-EDTA complex in solution not only increases the

amount of La(III) adsorbed but increases the stability of the La(III)-surface bond and reduces the amount desorbed with 0.001 M $Ca(NO_3)_2$. The stability of the La(III) surface complex to desorption in the presence of EDTA is sphalerite > pyrite > galena > chalcocite; in its absence, the order is chalcocite > sphalerite > pyrite > galena.

The presence of a soluble organic complexing ligand should reduce the mobility of La(III) in porous media and its transport to groundwater in the percolating soil solution. Binding mechanisms are proposed to account for this preferential binding behavior.

KEY WORDS: Adsorption mechanisms, precipitation, complexation, chalcocite, galena, pyrite, and sphalerite.

INTRODUCTION

The lanthanides, a set of important elements, are extensively dispersed among rocks and minerals. Lanthanides are surface mined, similar to other ores. Sulfide minerals may be present in the same ore deposit. Lanthanides are widely used in commerce. Agriculturally, they are found in fertilizers and in pharmaceuticals used in veterinary medicine. Industrially, they are used in metallurgy and in the porcelain industry. China provides an important source of lanthanides in the world market. Leachate from lanthanide tailing piles may pose a threat to both surface and groundwater quality. The degree of bioaccumulation and the toxicity of lanthanides to biota, however, is poorly understood.

Lanthanides have general characteristics similar to the alkaline earth metals. Lanthanum -- the first element in the lanthanide series -- is present in solution only in the trivalent state, is diamagnetic, and is water soluble in the halide salt form. Its oxides, hydroxides, carbonates and phosphates are only sparingly soluble in water (Moeller, 1973).

Trivalent lanthanum is not hydrolyzed under pH 6.0 and, therefore, is a useful element for studying the effect of valence and the nature of the free hydrated ion on sorption processes. Lanthanum also can be used as a surrogate to study the behavior of trivalent aluminum and chromium because, except in very acidic environments, these elements hydroylyze to polynuclear hydroxycomplexes and finally form oxy-hydroxy precipitates (Moeller, 1972). It can be used for an example of exchange adsorption of heavy metal ions on minerals.

The sulfide minerals are important constituents of soils, sediments, and aquifer materials and their interaction with the lanthanides is unknown. The transport and transformation of lanthanides in the environment is an important research area.

In this paper, we report our studies of the adsorption and desorption behavior of lanthanum on four sulfide minerals as influenced by pH and the presence or absence of a soluble organic complexing agent, the disodium salt of ethylenediaminetetraacetic acid (EDTA).

MATERIALS AND METHODS

Sulfide Mineral Preparation. Pyrite, sphalerite, galena, and chalcocite were obtained from the Ward's Natural Scientific Establishment. All minerals were examined by X-ray powder diffraction and only minor impurities were found (less than 5%). The minerals were crushed and sieved into four fractions using a nested set of Tyler standard stainless-steel mesh sieves. The surface area was determined by the ethylene glycol monoethyl ether method (EGME method) as described by Heilman et al. (1966). Physical data for the four sulfide minerals are given in Table 1.

Adsorption Isotherm Methodology

Stock solutions of $La(NO_3)_3$ with a concentration range of $1x10^{-3}$ to $1x10^{-5}$ moles/liter were prepared using Fisher Certified grade chemicals and nanograde quality deionized water. Calcium nitrate was used to provide a background electrolyte and to simulate the median concentration of calcium in groundwater (Brown et al. 1986). The required working solution was prepared by dilution of the stock solution. Six different initial concentrations ($2x10^{-5}$ M to $2x10^{-4}$ M) of the $La(NO_3)_3$ usually were prepared. The nitrate salt was used to limit or prevent the formation of ion pairs in solution.

A mixture of 0.5 ml of 1.0×10^{-4} M $La(NO_3)_3$ and 24.5 ml of 0.001 M $Ca(NO_3)_2$ solution was prepared, then 0.200 g of sulfide mineral was added. The pH of the solution was adjusted by adding 0.10 N NaOH and 0.10 N HNO_3.

After measuring the pH, the solution was placed in a wrist

shaker for 24 hours in a climate-controlled room at 25°C. Preliminary experiments showed that equilibrium was generally reached in 24 hours. Removal from the climate-controlled room was followed by centrifugation at 15000 rpm for 20 minutes in a temperature- controlled centrifuge at 25°C.

A 20-ml aliquot was analyzed on a Perkin-Elmer plasma II inductively coupled plasma emission spectrometer (ICP). In addition to the equilibrium concentration of La(III), the concentration of sulfur and the major cations in each of the sulfide minerals suspensions were measured. Analytical values represent the average of three replicate analyses on the ICP. All samples were run in duplicate. In all cases, a mineral and a solution blank were included and adjustments were made for any adsorption onto the tube wall. Initial pH and equilibrium solution pH were determined using a combination glass electrode and an Orion 940 expandable ion meter.

Effect of pH on Adsorption

Parallel sets of solutions were made up containing 125 ml of a combined solution of 1×10^{-3} M $La(NO_3)_2$ and 1×10^{-3} M $Ca(NO_3)_2$ (background electrolyte to simulate the median concentration of groundwater as found by Brown et al. 1986), and the pH was adjusted to the desired value with 0.10 N NaOH or 0.125 N HCl. Values for pH ranged from a low of 2.0 to a high of 10. To this solution, 1.000 g of air-dry sulfide mineral was added, and the suspension was shaken for 24 hours at 25°C in a climate- controlled room, then removed and centrifuged at 15000 rpm for 20 minutes at 25°C.

A 20 ml aliquot of the supernatant was removed and the pH and Eh were measured with a combination glass electrode and a platinum electrode on an Orion 940 expandable ion meter, respectively. The remainder of the supernatant was used in measuring the equilibrium concentration of the La(III), the sulfur, and the major cation present in each suspension. Appropriate solution and mineral blanks were run. In certain circumstances, the pH of the equilibrium solution was increased by adding 0.10 N NaOH and shaking the solution for 4 hours. This procedure was repeated until the desired pH was obtained. The mineral was dried at 100°C and weighed. This weight was used to correct the air-dry weight value to the oven-dry value.

Effect of EDTA on Lanthanum Sorption

A 25-ml solution of 3.92×10^{-4} M EDTA was mixed with 0.5 ml of 1.0×10^{-4} M $La(NO_3)_3$ and 0.2 grams of sulfide mineral. The solution was shaken for 24 hours at 25°C, then centrifuged for 20 min at that temperature. After centrifugation, the supernatant was analyzed by ICP.

Desorption of Lanthanum

To each tube containing the La(III)-mineral complex was added 25 ml of desorbing agent (1.0×10^{-4} M EDTA). The solution was put in a wrist shaker again for 24 hours in a climate-controlled room at 25°C. Then the tube was placed in a temperature-controlled (25°) centrifuge and centrifuged for 20 minutes at 10000rpm. The solution was analyzed by ICP.

Calculation of Partition Coefficients (Kd)

The partition coefficient is defined as the amount of metal adsorbed per gram of sulfide mineral (in umoles/g) divided by the equilibrium metal concentration (in umoles/L). The units are liters/gram. To compare La(III) adsorption on sulfide minerals as a function of treatment, an equilibrium concentration was selected and the appropriate Kd was calculated. The criteria for selection of the appropriate equilibrium concentration was that it either be a midrange equilibrium concentration, or, if this was not feasible, the highest metal equilibrium concentration possible for that particular treatment.

Application of Adsorption Isotherms

Attempts to describe the phenomenon of adsorption have used linear adsorption isotherms, Freundlich isotherms, Langmuir isotherms, Langmuir two-surface isotherms, Competitive Langmuir isotherms, and variety of first-order kinetic sorption models. These models were reviewed at length by Travis and Etnier (1981). The applicability of three adsorption isotherms will be evaluated:

1. Linear adsorption isotherms

$$S = (Kd) * (Ce)$$

where S = amount of metal adsorbed by the sulfide mineral

Ce = equilibrium concentration of metal in the reacting solution

Kd = distribution coefficient

If we plot S vs. Ce, we will get a linear equation, $y = Bx + A$.

2. Freundlich isotherms

The isotherm is defined by the nonlinear relationship

$$F = (Kf)*(Ce)^{1/n}$$

$$\log F = \log(Kf) + (1/n)*[\log(Ce)]$$

$$a = \log(Kf),\ b = 1/n$$

where Kf and n are constants and depend upon the nature of the adsorbent (e.g., sulfide mineral) and adsorbate (e.g., metal characteristics) and the temperature. The linear form of the equation is log S = log Kf + n log C. n, therefore, represents the slope of the line and log Kf is the intercept. The two constants, Kf and n, encompass all factors affecting adsorption from solution properties of the solvent and the equilibria between adsorbate-solvent, absorbate-adsorbent and adsorbent-solvent.

3. Langmuir Isotherm

The isotherm can be written

$$F_M = \frac{(F^o_M) * (K_M) * (C_e)}{1 + (K_M) * (C_e)}$$

where F_M = quantity of metal M adsorbed

F^o_M = adsorption maxima of F_M

K_M = constant measure of the affinity of metal M for the sulfide mineral surface. K_M depends on the pH value and ionic strength of the soil solution.

C_e = equilibrium concentration of metal M

and $$\frac{1}{F_M} = \frac{1 + K_M * (C_e)}{(F^o_M) * (K_M) * (C_e)}$$

$$= \frac{1}{(F^o_M) * (K_M) * (C_e)} + \frac{1}{K_M}$$

$$\frac{1}{F_M} = \frac{c}{C_e} + d$$

where $$c = \frac{1}{(F^o_M) * K_M}$$

$$d = \frac{1}{(K_M)}$$

A good fit of adsorption data to a particular adsorption isotherm(s) does not constitute defacto proof of any specific binding mechanism because it is not possible to distinquish between complete adsorption and precipitation.

RESULTS AND DISCUSSION

Adsorption Isotherms of Lanthanum

Figure 1 shows the experimental adsorption isotherms of lanthanum on the four sulfide minerals. The adsorption reaction was conducted at or near the pH of the mineral's natural acidity (Table 1). A comparison between the extent to which the four sulfide minerals adsorbed La(III) was obtained by selecting a metal equilibrium concentration midway in the range and picking off the appropriate amount of metal adsorbed for each mineral. The isotherm generally indicates that the adsorption amount increases with increasing equilibrium solution concentration.

The regression coefficients in Table 2 show that the adsorption process is very complex and varies with the nature of the mineral. Adsorption of La(III) on pyrite can be fitted by any one of models above, the regression coefficients being larger than 0.95. Adsorption on chalcocite, however, follows the Langmuir formulate; adsorption on sphalerite is described by a linear relationship.

The order of La(III) adsorption on sulfide minerals based on Kd is pyrite (Kd=0.030) > chalcocite (Kd=0.02) > galena (Kd=0.013) > sphalerite (Kd=0.005). Pyrite's affinity for La(III) is stronger than the other minerals. From an environmental view, pyrite is an important constituent affecting the transport and transformation of lanthanum in soils, sediments, and aquifers.

Table 1. Physio-chemical Properties of Four Sulfide Minerals (Lin et al. 1988)

Properties	Mineral Type: Pyrite	Galena	Chalcocite	Sphalerite
Formula	FeS_2	PbS	Cu_2S	ZnS
Part.Size* (u)	<53	<53	<53	<53
Surface Area(m^2/g)	4.8	2.0	3.1	2.5
Exchange Sites (umoles/g)	95.5	74.5	55.1	79.9
pH_{zpc}	4.41	7.44	7.47	7.10
pH_n**	2.46	5.98	6.06	5.62
pK_{a1}	3.50	5.26	5.25	5.08
pK_{a2}	5.32	9.62	9.68	9.13
pK_{a3}	9.81			
Solubility product	$1.0x10^{-17}$	$3.4x10^{-28}$	$2x10^{-47}$	$1.2x10^{-23}$
mineral *** solubility	$4.9x10^{-04}$	$8.6x10^{-05}$	$1.19x10^{-14}$	$6.5x10^{-05}$

* The size of particles is the size of sieve in the experiment.

** pH of the natural mineral in water; a solid to water ratio of 1.1 was used to measure pH.

*** The mineral solubility is the solubility in water at 25°C, (g/100ml), (g mol/kg).

Table 2. Regression Coefficients and Parameters of Three Adsorption Isotherm Equations

	Type of Adsorption Isotherm								
	Linear			Freundlich			Langmuir		
	r	A	B	r	a	b	r	c	d
Pyrite	0.992	-0.418	3.055	0.991	0.373	1.184	0.996	-0.054	0.507
Sphal.	0.918	-0.141	0.692	0.882	-0.122	0.806	0.707	0.404	0.777
Chal.	0.970	1.972	1.383	0.972	0.548	0.530	0.949	0.121	0.135
Galn.	0.775	0.684	0.711	0.731	-0.068	0.983	0.999	0.826	0.634

The Dependence of Adsorption on pH

The Figures 2 through 4 demonstrate that adsorption of lanthanum on sulfide minerals increases dramatically with increasing solution pH and metal concentration. Pyrite has a greater affinity for La(III) than does galena, particularly in the pH range of 4.2 to 7.1. The affinities are similar to those observed by Benjamin (1979) and Benjamin and Leckie (1981) for the adsorption of heavy metals on hydrous oxide surfaces.

This S-shaped curve in Figure 2 is called the adsorption edge and shows that complete adsorption occurs within plus or minus 1 to 2 pH units of the established concentration. The pH_{50} is defined as the pH at which 50% of the amount of the metal added is adsorbed. Lin et al. (1988) determined the adsorption edge and calculated the pH_{50} for several metals on different sulfide minerals. The pH_{50} for La(III) is 6.4 on galena and 5.3 on pyrite. Increases in the initial metal concentration raise the pH_{50} value. For pyrite, pH_{50} increases from 5.3 to 6.1 as the concentration changes from 6.7×10^{-4} to 1.2×10^{-4} moles/liter. Therefore, the pH_{50} value is related to the metal

type and concentration and to the nature of the sulfide surface. The hydrolysis constant of the metal and the intrinsic acidity constants of the sulfide mineral surface are the major contributing factors.

Figures 5 and 6 show that lanthanum speciation rarely occurs until the solution reaches pH 6.2. The hydrolyzed lanthanum in our study occurred as a small fraction of the total lanthanum concentration when the pH was less than 6.0. Lanthanum at a concentration of 1×10^{-4} M precipitates at pH 8.0 (Figure 6). This is in line with the value of 7.82 cited by Moeller (1972). A comparison of the data in Figures 3 and 6 shows that the cause of adsorption of lanthanum on the sulfide mineral is neither hydrolysis nor precipitation. We believe it to be complexation, i.e., Lewis acid and base reaction with, principally, the hydrated free ion being adsorbed mainly due to electrostatic interactions.

The complexation adsorption model by Stumm et al. (1976) can be used to fit the data and explain the results. In this model, the hydrous oxides are treated as diprotonic acid. We also treated three of the sulfide minerals as diprotonic acids (Table 1). The acid-base titration curve of galena is shown in Figure 7. The intrinsic acidity constants illustrate that the acidity of the sulfide mineral is stronger than the hydrous oxides (Table 3). The acidity constants of sulfides more closely approximate that of acetic acid . The titration curve inflection is steeper than that of the oxides.

Table 3. Comparision of Intrinsic Acidity Constant for Oxides and Sulfide Minerals

System*	pKa1	pKa2	System**	pKa1	pKa2
$-Al_2O_3/NaCl$	5.7	11.5	FeS_2	3.50	5.32
$-FeOOH/KNO_3$	4.2	10.8	PbS	5.26	9.62
-FeOOH/NaCl	4.9	No	Cu_2S	5.25	9.68
$Fe_2O_3.H_2O/NaNO_3$	5.1	10.07	ZnS	5.08	9.13
$TiO_2/LiNO_3$	2.6	9.0	Acetic acid ***	4.75-5.015	
TiO_2/KNO_3	2.6	9.0			
SiO_2/KCl	No	7.2			

* Davis and Leckie (1978)
** Lin et al. (1988)
*** Kotrly and Sucha, (1985)

In the complexation adsorption model cited, it was presumed that the metal ions were adsorbed on the hydroxyl groups. In this paper, we propose that the metal is complexed with the thio-group. The thio-group can be dissociated as follows

$$MeSH_3^{+2} = MeSH_2^{+} + H_3O^{+}$$

$$MeSH_2^{+} = MeSH + H_3O^{+}$$

$$MeSH = MeS^{-} + H_3O^{+}$$

The reaction of the heavy metal ion with the surface of sulfide mineral is given by:

$$MeSH + M^{+z} \overset{K_{c1}}{=} MeSM + H_3O^{+}$$

$$2\,MeS^{-} + M^{+z} \overset{K_{c2}}{=} 2(MeS)M$$

(where z = valence)

The amount of metal absorbed is:

$$[Mbound] = [MeSM] + [2(MeS)M]$$

$$\frac{[Mbound]}{[M]} = K_{c1}\frac{[MeSH]}{[H^{+}]} + \frac{2K_{c2}\,[MeS^{+}]^2}{[MeSM]}$$

Speciation at the Sulfide Surface

Species that may be present at the sulfide surface or in the interfacial volume are:

Specie #	Surface specie type
1	MeS
2	S_5^{-2}
3	$Me(OH)(H_2O)^{-1}$
4	$Me\ (OH)_2(H_2O)_{ppt}$
5	$Me\text{-}SH_3^{+2}$
6	$Me\text{-}SH_2^{+1}$
7	Me-SH
8	$Me\text{-}S^-$

(where Me = host metal in sulfide mineral)

Specie number 3 is obtained in the following manner

(a) Mineral Dissolution:

$$MeS \text{ <===> } Me + S^{-2}$$

(b) Metal Hydrolysis:

$$Me + H_2O \text{ <===> } [Me(OH)_x(H_2O)_{n-x}]^{2-(n-x)} \text{ (specie \#3)}$$

(where n = coordination number)

Specie number 2 is obtained in the following manner

(a) Sulfur Oxidation:

$$8\ S^{-2} \text{ <===> } S_8^{o} + 16e^-$$

(b) Sulfide Hydrolysis (Jellinek 1968):

$$S^{-2} + H_2O \text{ <===> } HS^- + OH^-$$

$$HS^- + H_2O \text{ ---> } H_2S + OH^-$$

(c) Polysulfide formation:

$S_8^{o} + 2\ HS^{-} \text{ <===> } 2\ S_5^{-2}$ (specie #2)

(G. M. Bancroft, personal communication, Jean and Bancroft 1986, and Gould 1955)

Speciation in Solution

The various lanthanum species present in solution include:

$$La(III) + 10H_2O \text{ <===> } [La(H_2O)_{10}]^{+3}$$

Specie (I)

$$\text{Specie (I)} \text{ <===> } La(OH)_3 \text{ ppt} + 3H_3O^{+}$$

Specie (II)

$$CO_2 \text{ <===> } HCO_3^{-} \text{ <===> } CO_3^{-2} + H_3O^{+}$$

$$\text{Specie (I)} + CO_3^{-2} \text{ <===> } La_2(CO_3)_3 \text{ ppt}$$

Specie (III)

$$\text{Specie (I)} + HCO_3^{-} \text{ <===> } La(HCO_3)_3 \text{ ppt}$$

Specie (IV)

$$\text{Specie (I)} + Na_2H_2EDTA \text{ <===> } [La(H_2O)_4EDTAH].3H_2O +$$

Specie (V)

$$2H_3O^{+} + 2\ H_2O + 2\ Na^{+}$$

$$\text{Specie (V)} \text{ <===> } [La(H_2O)_4EDTA]^{-1}.3H_2O + H_3O^{+}$$

Specie (VI)

Specie V is predominant below a pH of 3.0 and becomes a minor specie above a pH of 3.4. The free hydrated ion is a very minor specie in the presence of EDTA above pH 2.0 in specie V. Lanthanum is a 10 coordinated specie, i.e. in decahedral configuration (Moeller 1972) presumably with EDTA.

Effect of Ligand on the Adsorption of Lanthanum

The presence of an organic ligand in solution dramatically influences the adsorption characteristics of the heavy metal ion to mineral surfaces. Figure 8 indicates that the effect of the organic ligand (EDTA) on adsorption is very important. Comparison of Figure 1 with Figure 8 and Kd calculation shows that the adsorption amount increases about fivefold to tenfold in the presence of the complexing agent. The order of adsorption for pyrite and chalcocite in presence of EDTA is reverse to that in absence of EDTA.

La(III) is a hard Lewis acid and EDTA is a hard Lewis base (Jensen 1980); the two, therefore, would be expected to form a stable complex. This can be seen in Table 4. La(III) forms a less stable complex with NTA (Moeller 1973). La(III) should bind with EDTA, NTA and other carboxylate acids primarily by electrostatic interactions; little evidence exists for any covalent interactions (Moeller 1973).

Based on the stability constants of the metal complexes by EDTA, as shown in Table 4, the sequence of adsorption in the presence of EDTA may be similar to the order of stability constants of the metal-EDTA complexes (the metal being the major cation present in each of the sulfide minerals).

Table 4. The Stability Constants for EDTA-Metal Complexes *

Stability Const.	Ca(II)	La(III)	Zn(II)	Pb(II)	Cu(II)	Fe(II)	Fe(III)
LogK1	11.4	15.5	17.0	18.5	19.5	14.32	25.1
LogK2	3.5	2.0	3.2	3.5	3.7	2.75	1.3

* after Kotrly and Sucha (1985).

Adsorption Mechanisms

Several binding mechanisms can be postulated for binding both the metal and the metal-ligand complex to the sulfide surface. These include four mechanisms proposed by Bowers and Huang (1986):

1) Metal-ligand complex bound to sulfide-ligand complex

(a) $M + L_1 \text{ ---> } ML_1$

(b) $MeS + L_2 \text{ ---> } MeSL_2^{-2}$

$ML_1 + MeSL_2^{-2} \text{ ---> } MeS\text{--}L_2\text{--}ML_1$

where M = metal

L_1 = EDTA

L_2 = another ligand like $La(OH)^{+2}$

MeS^- = metal sulfide surface

Me = host metal of the sulfide mineral

2) Metal of the metal-ligand complex bound to S^{-2} surface site

$MeS^- + ML_1 \text{ ---> } MeS\text{--}ML_1$

3) Ligand of the ligand-metal complex bound to the metal constituent of the sulfide mineral

$MeS^- + ML_1 \text{ ---> } SMe\text{--}L_1M$

4) Bidentate complex

$MeS^- + ML_1 \text{ ---> } MeS\text{--}M\text{--}SMe\text{--}L_1$

Stable 1:1 metal chelates can be formed between EDTA and lanthanum. Compared to the free hydrated ion with which it is in equilibrium, the metal chelate adsorbs preferentially onto the metal sulfide surface. The free hydrated trivalent ion, La(III), also may be adsorbed, but not the hydrolysis product. The

solvated La(III) ion is a weak acid and not extensively hydrolyzed. A strongly basic anion like S_n^{-2}, however, produces a sufficient concentration of hydroxide ions by hydrolysis such that precipitates of basic salts or hydroxides in contact with La(III) ions are produced (Moeller 1973). The adsorption of La(III) also may be due to the presence of the organic ligand. The preference of the EDTA ligand for the various metal/metal sulfide surfaces is pyrite < sphalerite < galena < chalcocite.

La_2O_3 and $La(OH)_3$ are nearly quantitatively insoluble in water, but, because of their relatively high basicity, dissolve readily in acids (Moeller 1973). These salts/hydroxides would only be present under an alkaline environment.

Stable 1:1 metal complexes with EDTA can be formed prior to the introduction of the sulfide mineral. These metal complexes can be adsorbed onto the mineral surface. The amount of lanthanum adsorbed is enhanced due to the presence of the chelate component of the metal-EDTA complex available on surface. On the other hand, the EDTA also can coordinate with the metal ion on the surface of sulfides, as Table 4 shows. With the exception of Fe(II), the stability constants of EDTA-host metal on surface sites are always higher than that of EDTA-lanthanum by around 2 to 4 orders of magnitude. Ligand bridges between the surface and the lanthanum ion, as discussed above, are hypothesized.

The formation of a lanthanum sulfide mineral might be an expected reaction. La_2S_3 can be formed, but only in nonaqueous systems and at elevated temperatures, and is readily hydrolyzable in the presence of water (Moeller 1973). Therefore, the reaction would not occur environmentally at the metal sulfide surface.

The reversal in the order of binding of Lanthanum between the two minerals may arise from the difference in the stability constants. The stability constant for EDTA-Fe(II) complex is smaller than that for the Cu(II)-EDTA. The configuration of EDTA-metal complexes at mineral surface needs to be studied in the future.

To induce the adsorption of a metal, the anion must be adsorbable - able to form a complex - and be capable of establishing a ligand bridge between the surface and the metal cation (Bowers and Huang 1986).

Figure 9 shows that the pH of solution influences the adsorption of the La-EDTA complex -- adsorption decreases with decreasing pH. The hydrogen ion competes very well for sorption sites on the surface of the sulfide minerals.

Desorption of Lanthanum from Sulfide Minerals

To understand the transport characteristics of lanthanum in the environment, the desorption behaviour needs to be studied. Figure 10 shows that the desorption of La(III) reaches equilibrium in 6 hours. The desorbate equilibrium concentration is different due to the difference in the amount adsorbed on pyrite. Figure 11 shows the relationship of the amount desorbed to the amount adsorbed. The amount desorbed increases when the amount adsorbed on pyrite increases. Desorption may reach a plateau value, however, when the adsorption amount increases. The reason for this may be hydrolysis and precipitation of the lanthanum ion, when the desorption concentration is around 1 ppm.

Figure 12 compares the effect of EDTA and background electrolyte on desorption of La(III) from pyrite; the result shows that more La(III) was desorbed by the background electrolyte -- $Ca(NO_3)_2$ -- than by EDTA. This phenomenon is consistent with the effect of EDTA on adsorption. The amount adsorbed increases in the presence of EDTA due to chemical complexation.

Figures 12 and 13 show that the sequence of lanthanum adsorption on pyrite (and probably other sulfides) may play an important role in desorption of the metal. In the case of lanthanum adsorption in absence of EDTA , the desorption by EDTA is easier than that for the desorption of La-EDTA complexes on sulfide. The extent of desorption is greater by about an order of magnitude. It illustrates that the EDTA will enhance the stability of lanthanum bound on the sulfide minerals.

Figure 14 shows that the stability of La-EDTA complexes on the sulfide minerals is different. The order of stability is sphalerite > pyrite >> galena > chalcocite (Figures 14 and 16). Conversely, the order of stability of lanthanum on the surface in the absence of EDTA is chalcocite > sphalerite > pyrite > galena (Figures 13 and 15).

SUMMARY AND CONCLUSIONS

The adsorption sequence of lanthanum alone on sulfide is pyrite > chalcocite > galena > sphalerite. The effect of pH on adsorption is very important. The pH_{50} of La(III) is 6.4 on galena; 5.3 on pyrite. The pH_{50} is not only dependent on the type of sulfide mineral, but also on the concentration of lanthanum present. The complexation mechanism explains the result.

EDTA can enhance the amount of lanthanum bound on sulfide minerals and can change the sequence of adsorption on sulfide minerals; the sequence of adsorption being chalcocite > pyrite > galena > sphalerite. The results show that the stability constant of La-EDTA complexes has a very important effect.

The adsorption configuration of the La-EDTA complex was proposed to describe the observed results. The desorption behavior of La(III) on sulfides was examined in the laboratory; on sulfides the stability of lanthanum is different from that of La-EDTA complexes. The stability of La-EDTA complexes at the surface is greater than that of the free hydrated lanthanum ion. The percent desorption of the La-EDTA complexes is an order of magnitude less than that of the lanthanum ion itself.

Sulfide minerals play an important role in the transport and transformation of lanthanum in the environment. Both pH and complexing organic ligands will influence the fate of lanthanum in soils, sediments and aquifer materials. The presence of soluble organic ligands in the soil solution or pore water and their complexation with lanthanum will decrease the mobility of

lanthanum through porous media because of enhanced adsorption to sulfide minerals. In the absence of soluble organic ligand, lanthanum adsorption will increase as the pH increases, and hydrolysis and polymerization will then occur resulting in precipitation above pH 7.8.

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REFERENCES

Benjamin, M. M. 1978. Effect of Competing Metals and Complexing Ligand on Trace Metal Adsorption at the Oxide/Solution Interface. Ph.D. Thesis. Stanford University, Stanford, CA. 241 p.

Benjamin, M.M. and James O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. J. Colloid and Interface Sci. 79:209-223.

Bowers, A.R. and C.P. Huang. 1986. Adsorption characteristics of metal-EDTA complexes onto hydrous oxides. J. Colloid and Interface Sci. 110:575-590.

Brown, D.S., R. Carlton, and L.A. Mulkey. 1986. Development of land disposal decisions for metals using MINTEQ sensitivity analysis. EPA/600/3-86/030. U.S. Environmental Protection Agency, Athens, GA.

Davis, J.A. and J.D. Leckie. 1978. Surface ionization and complexation at the oxide/water interface. J. Colloid Interface Sci. 67:90-107

Gould, E.S. 1955. Inorganic Reactions and Structure. Henry Holt and Company, New York, pp.283-296.

Heilman, M.D., D.L. Carter, and C.L. Gonzalez. 1966. The ethylene glycol monoethyl ether (EGME) technique for determining soil-surface area. Soil Sci. 100:409-413.

Jean, G.E. and G.M. Bancroft. 1986. Heavy metal adsorption on sulfide mineral surfaces. Geochem. et Cosmochimica Acta 50:1455-1463.

Jellinek, F. 1968. Sulphides. In: Inorganic Sulphur Chemistry. G. Nickless (ed). Elsevier Publishing Company, New York. pp.670-747.

Jensen, W.B. 1980. The Lewis Acid-Base Concepts: An Overview. Wiley and Sons, New York. p. 364.

Kotrly, S. and L. Sucha. 1985. Handbook of Chemical Equilibria in Analytical Chemistry. John Wiley & Sons, New York. pp. 175-177.

Lin, Y., G.W. Bailey and A.T. Lynch. 1988 (in preparation). Metal interactions at sulfide mineral surfaces. Part I. Acid-base characterization.

Moeller, T. 1972. Complexes of the lanthanides and actinides. In: Inorganic Chemistry Series 1, K.W. Bagnall (ed.). Butterworth, London and University Park Press, Baltimore.

7:275-298.

Moeller, T. 1973. The lanthanides. In: Comprehensive Inorganic Chemistry. A.F. Trotman-Dickenson (ed.). Pergamon Press, New York. 4:1-105.

Stumm, W., Hohl, H. and F. Dalang. 1976. Interactions of metal ions with hydrous oxide surfaces. Croat. Chemica Acta 48:491-504.

Travis, C.C. and E.L. Etnier. 1981. A review of sorption relationships for reactive solutes in soil. Journal of Environmental Quality. 10:8-17.

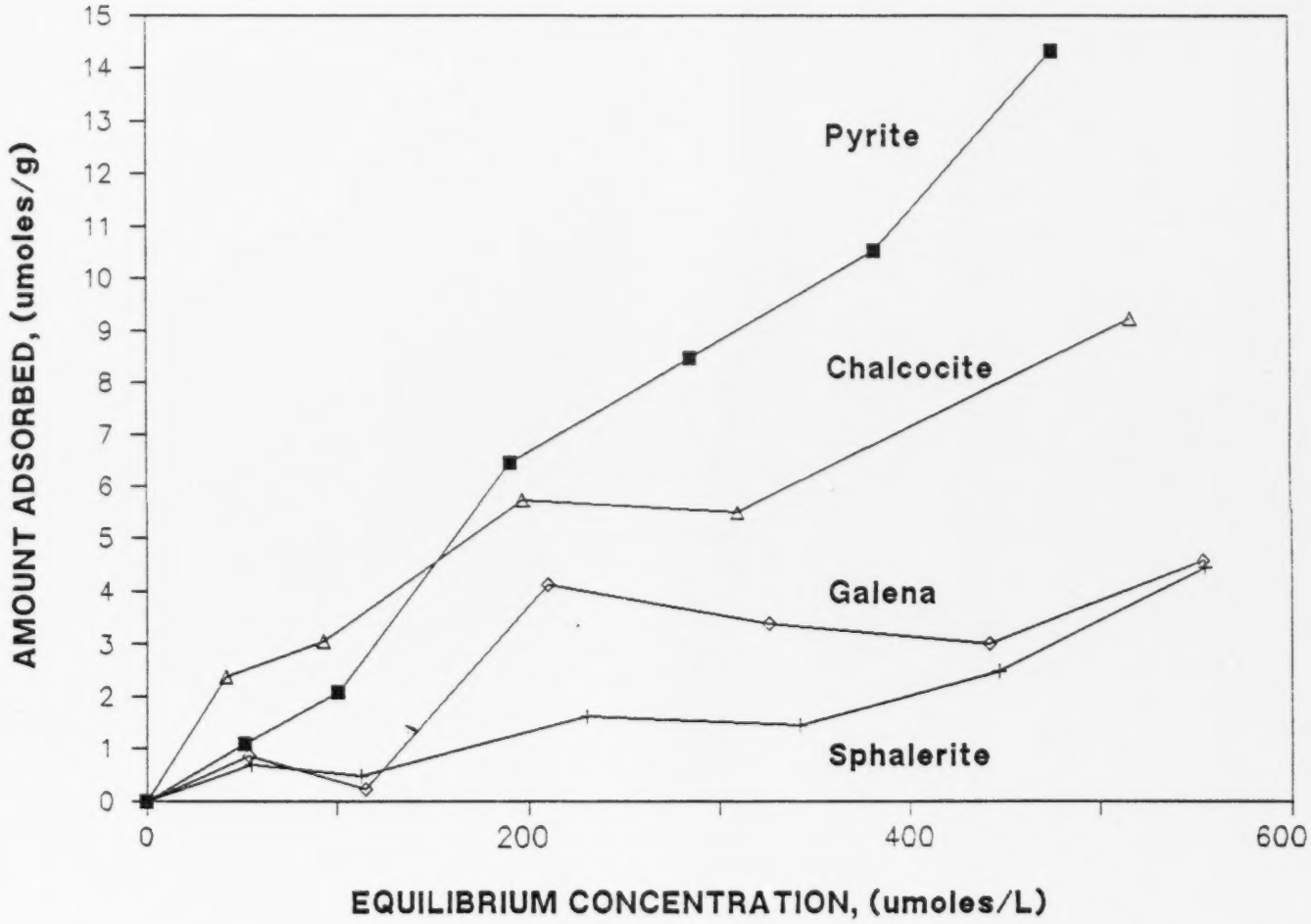

Figure 1. Adsorption Isotherms of La(III) on Four Sulfide Minerals

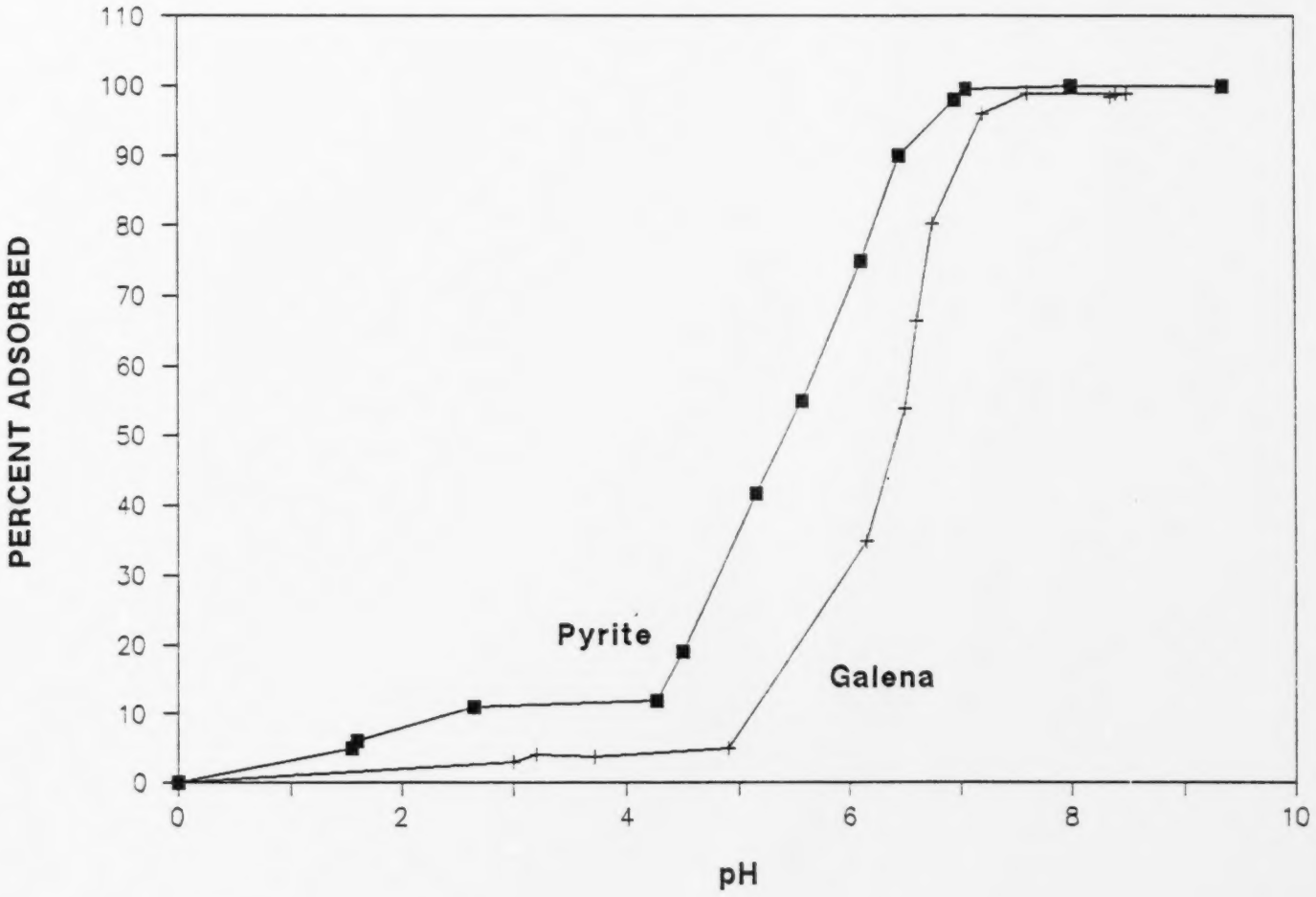

Figure 2. The Effect of pH on the Adsorption of La(III) by two Sulfide Minerals

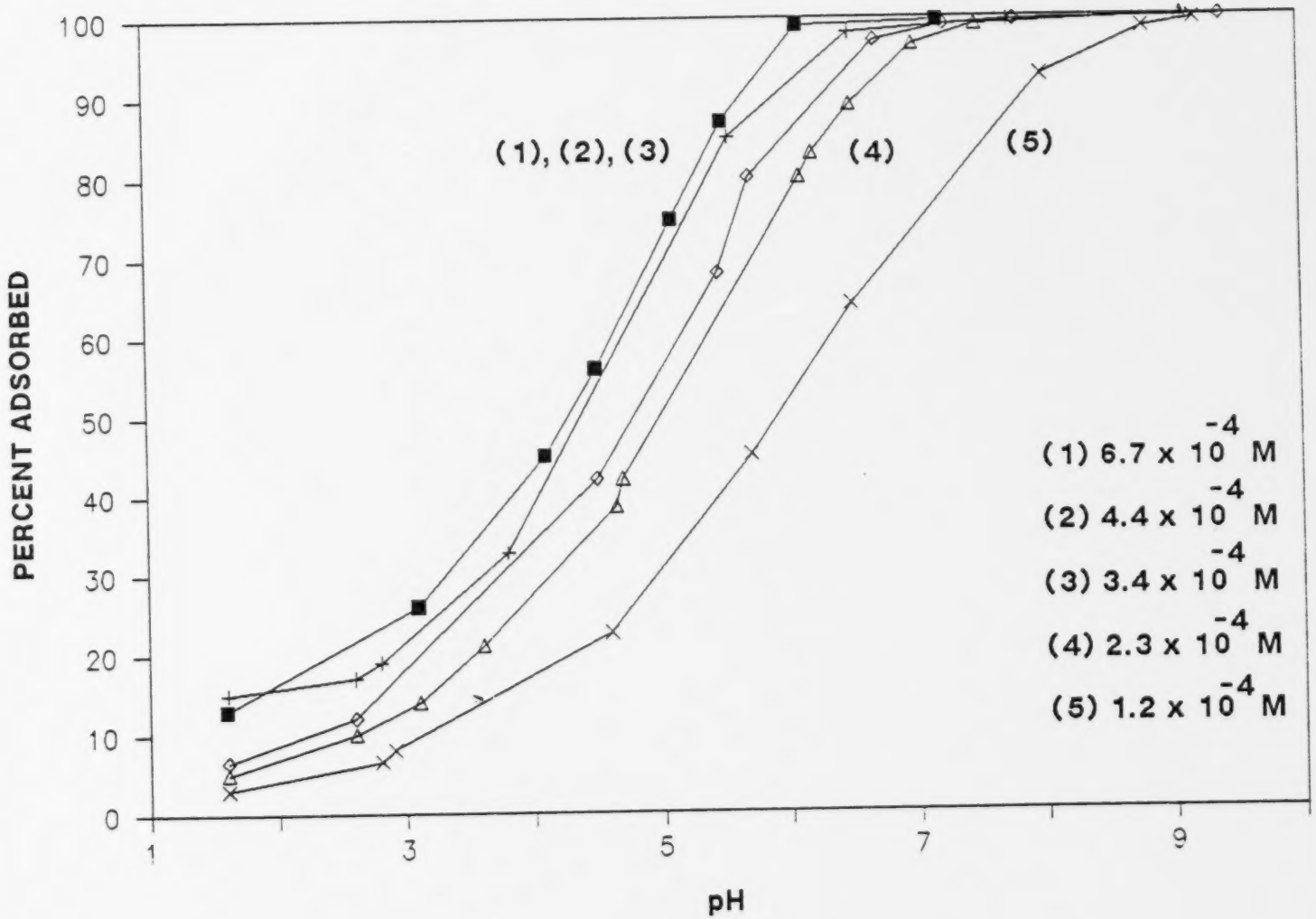

Figure 3. The Effect of pH and Metal Concentration on the Adsorption of La(III) by Pyrite

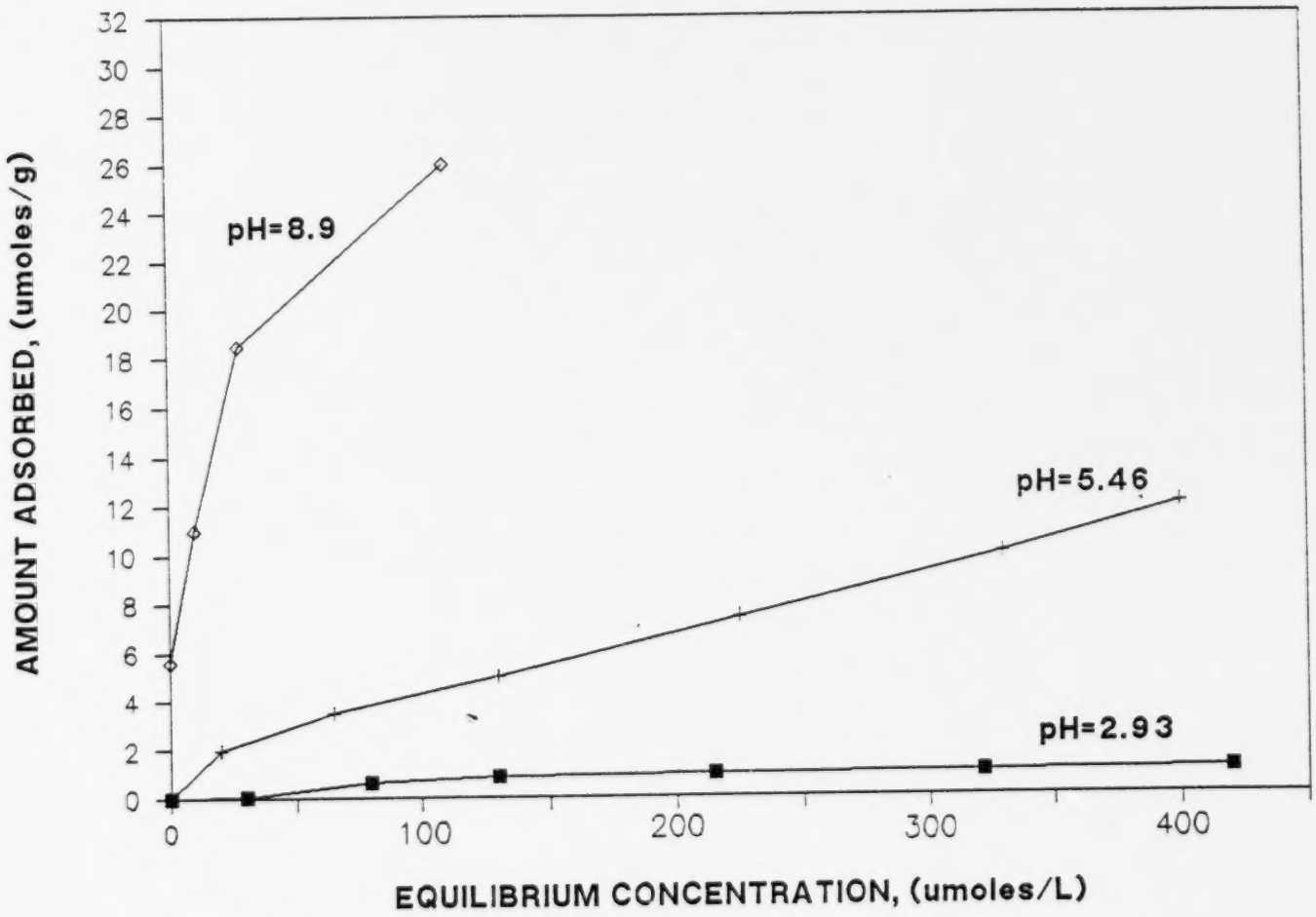

Figure 4. Adsorption Isotherms of La(III) on Galena at Different pHs

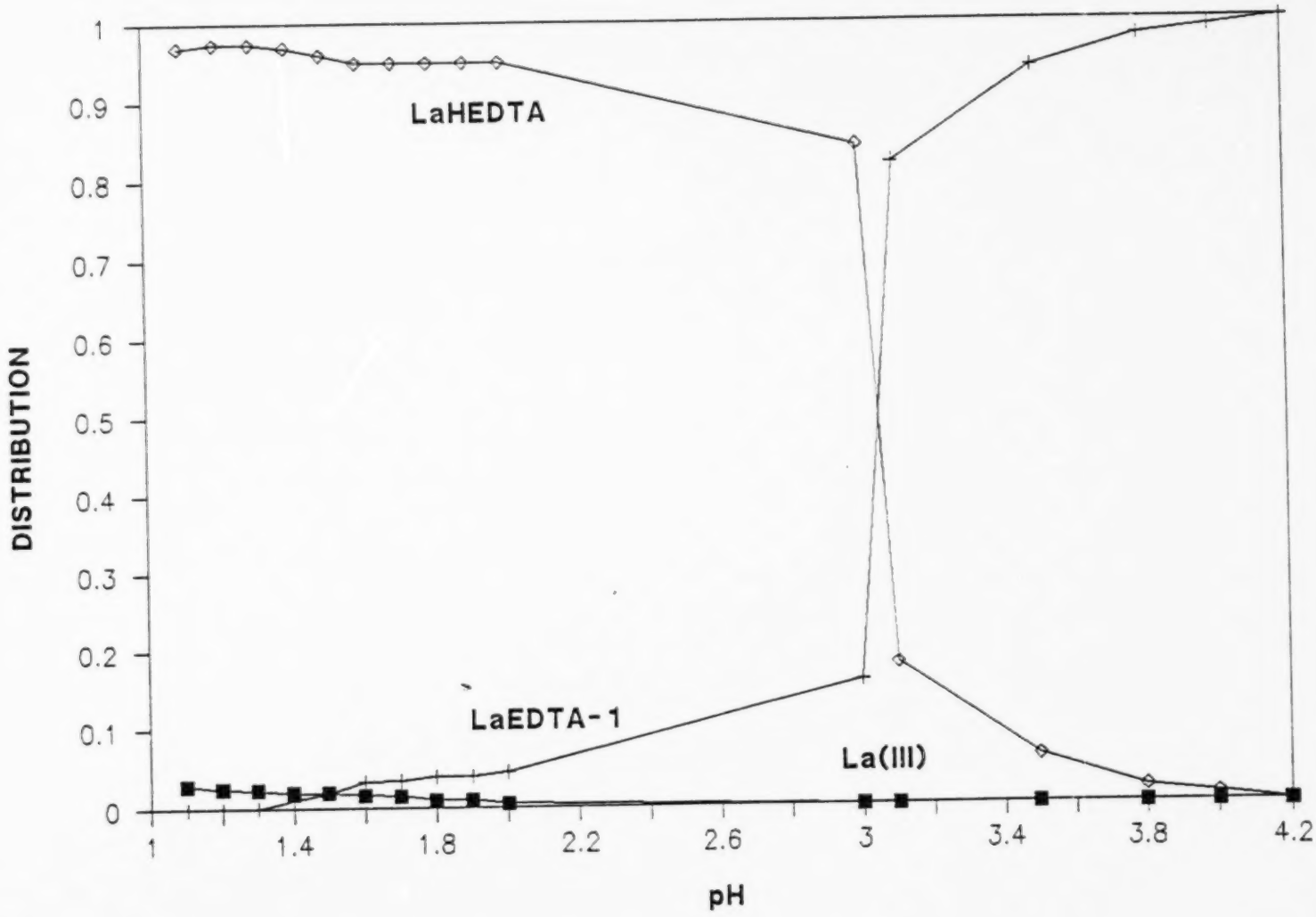

Figure 5. Species Distribution of La(III) - EDTA

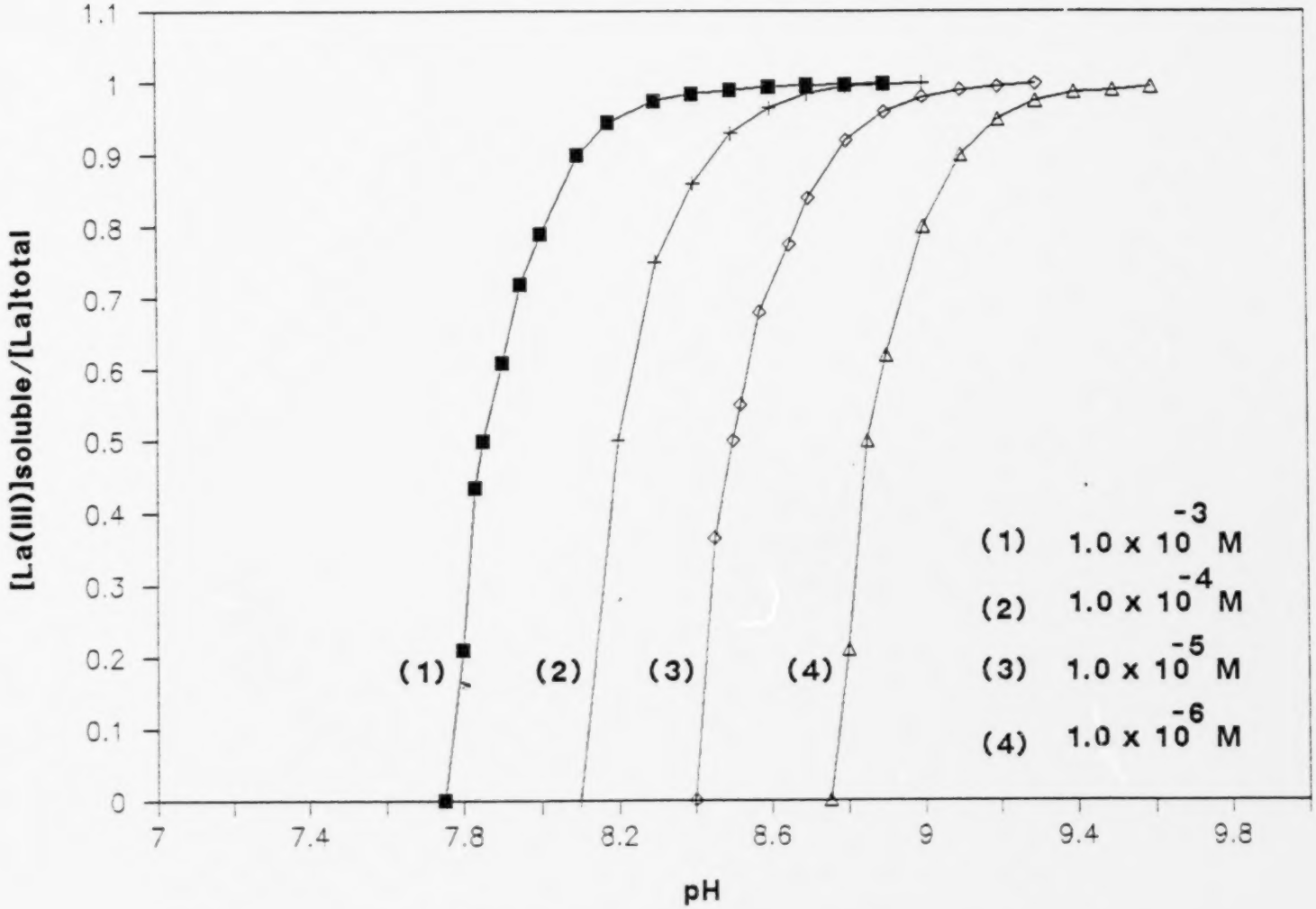

Figure 6. The Effect of pH on Precipitation of La(III) at Different Concentrations

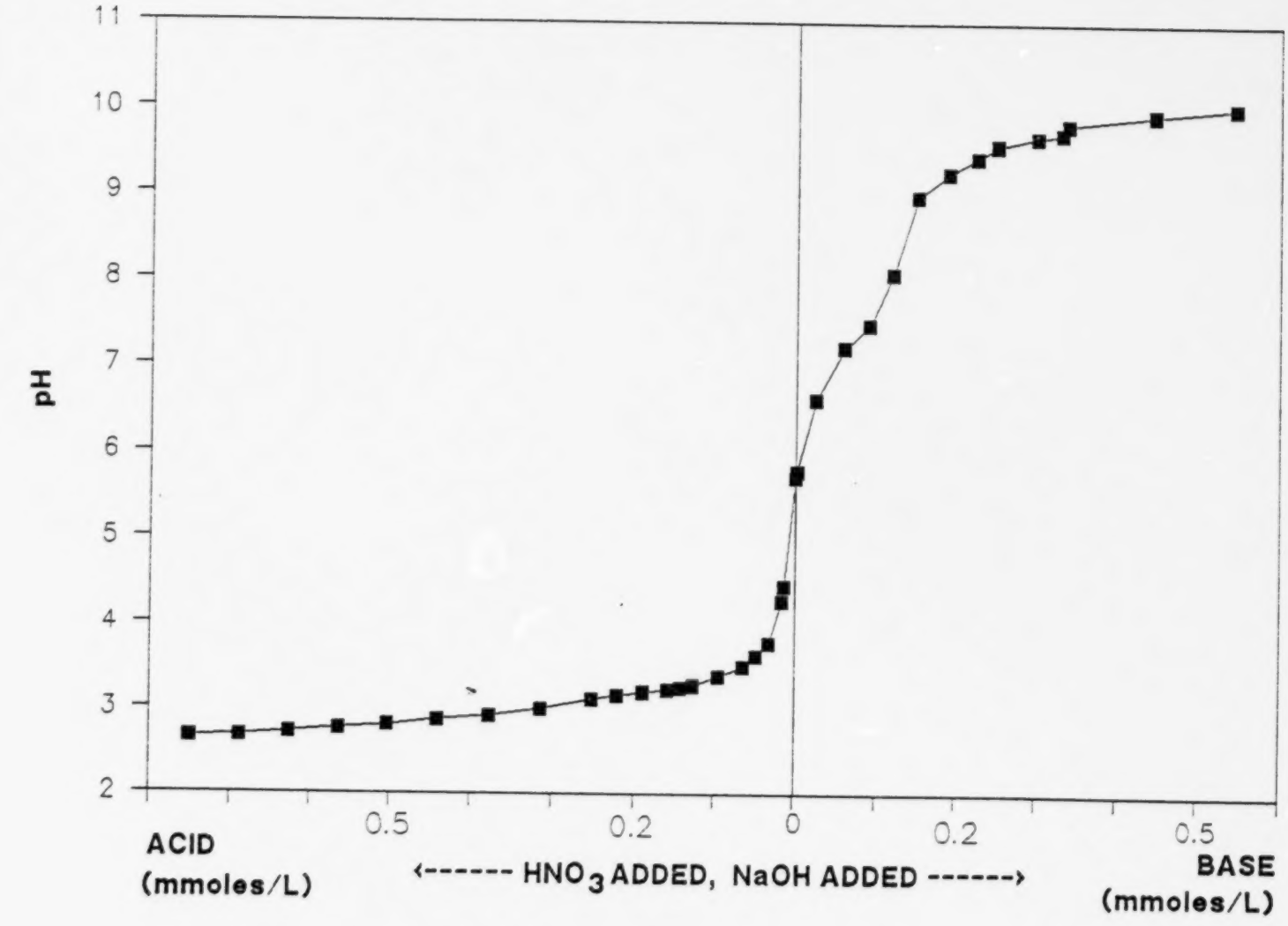

Figure 7. The Titration Curve of Galena

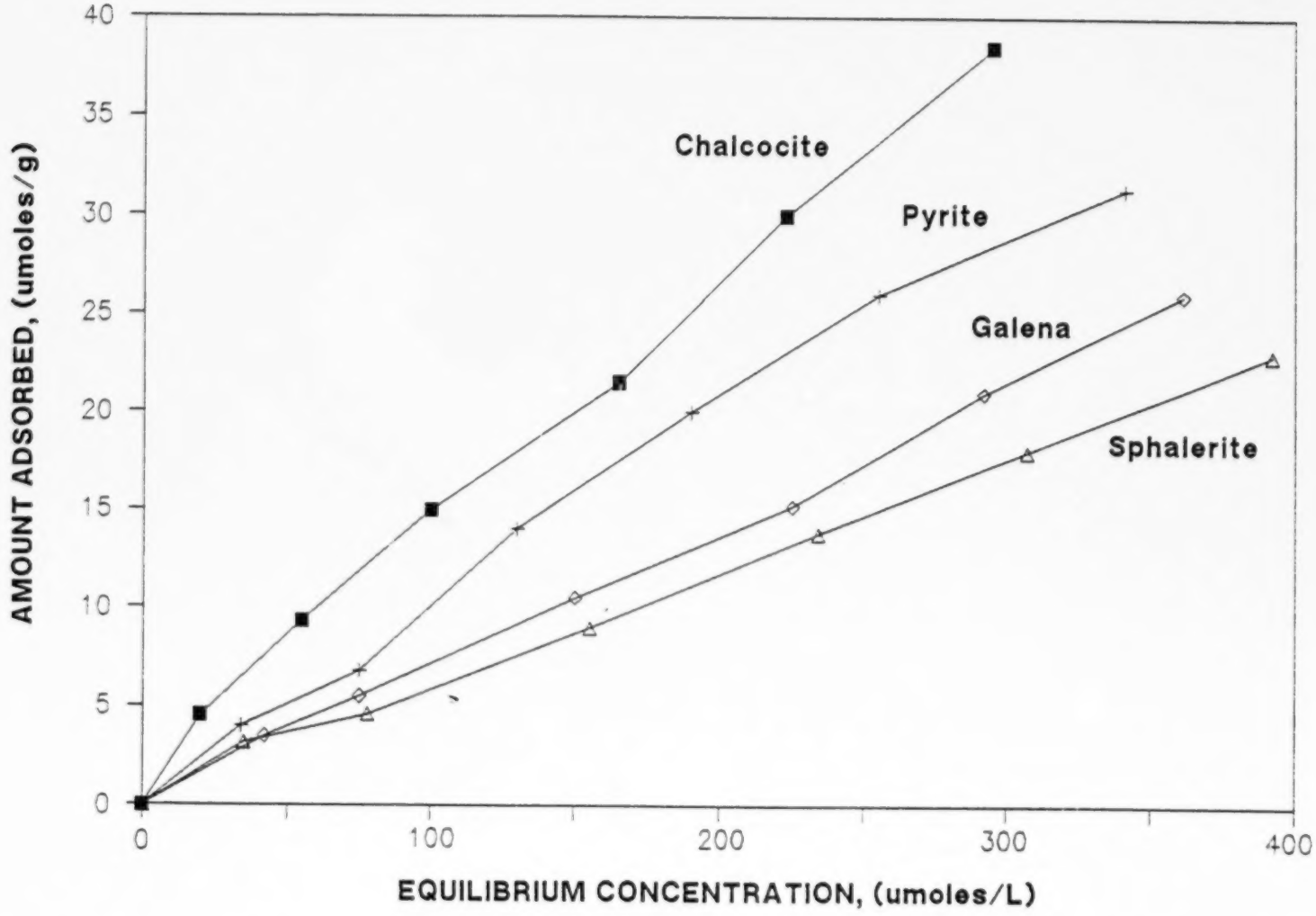

Figure 8. Adsorption Isotherms of La(III) - EDTA Complexes on Four Sulfide Minerals

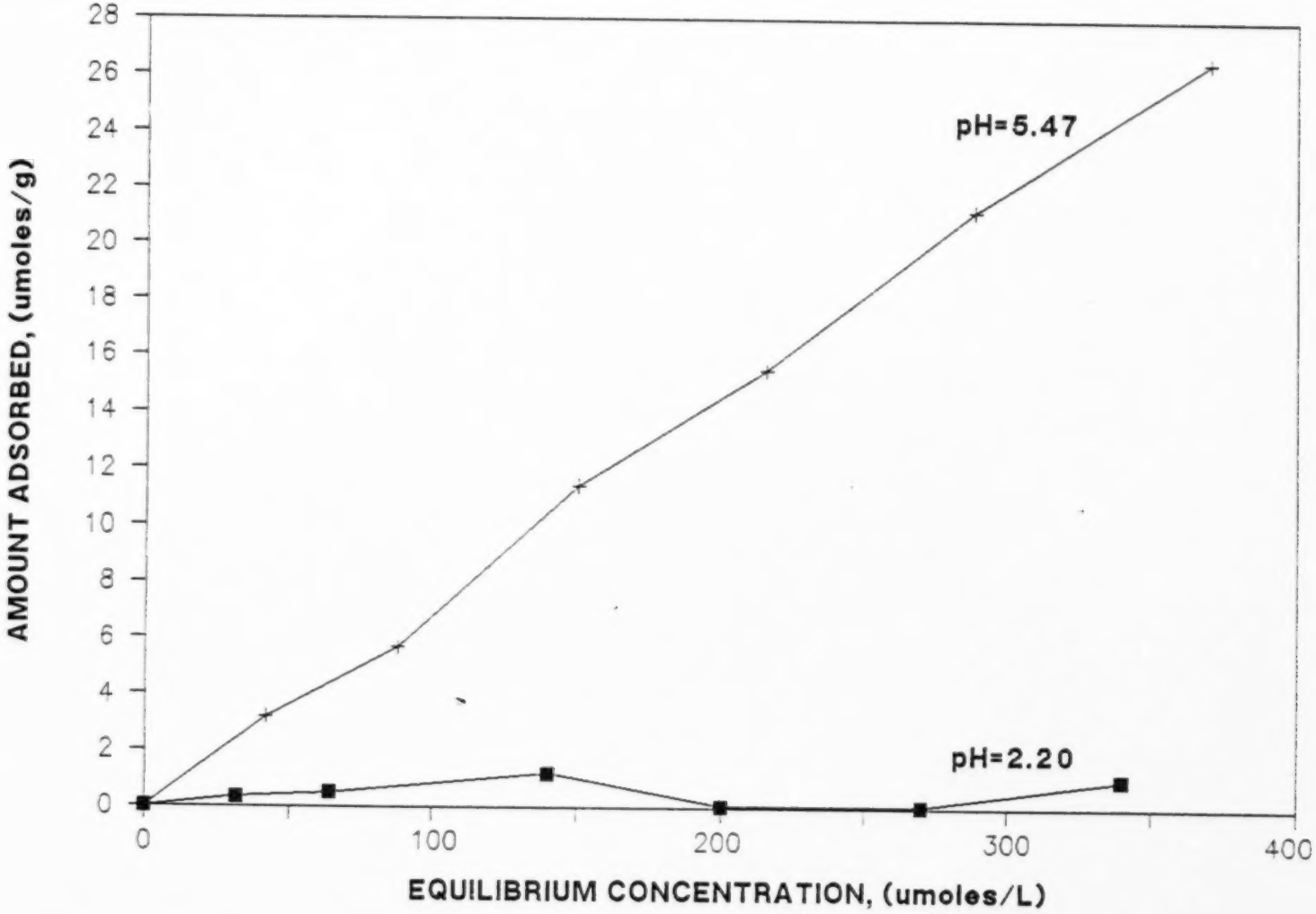

Figure 9. Adsorption Isotherms of La(III) - EDTA Complexes on Galena at Different pHs

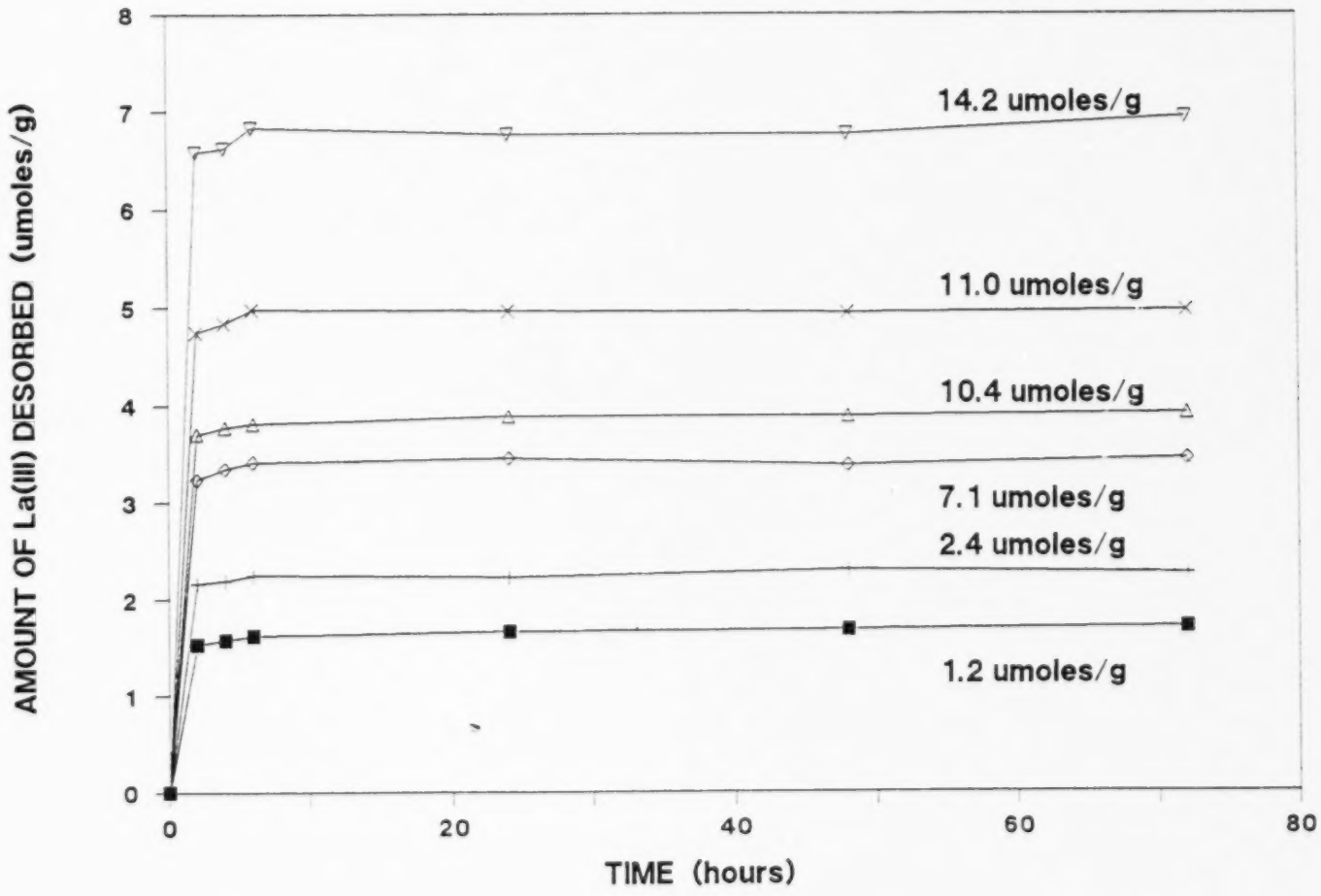

Figure 10. The Kinetics of La(III) Desorption from Pyrite by $Ca(NO_3)_2$ at Different Initial Adsorbed Metal Concentrations

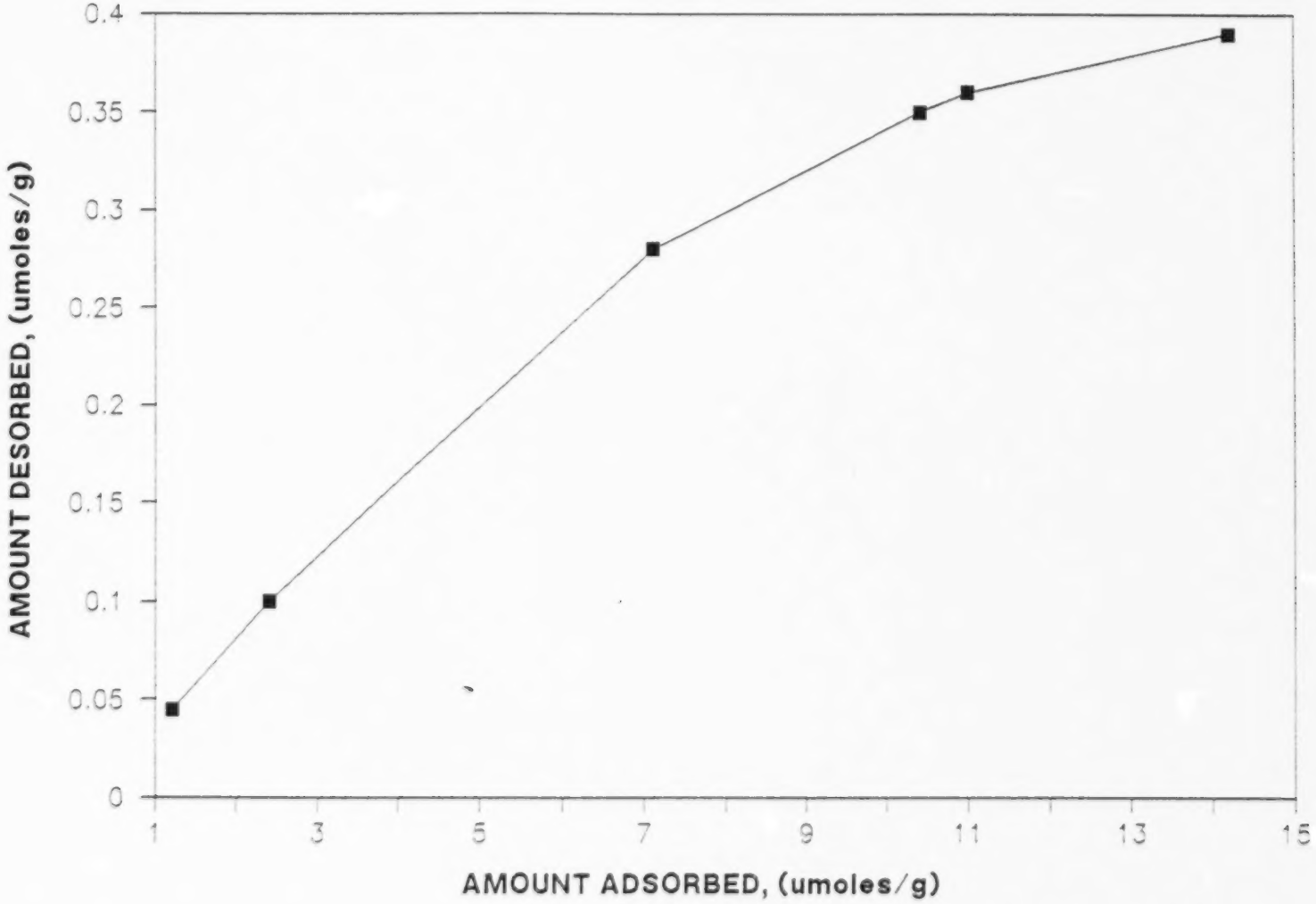

Figure 11. The Relationship Between Adsorption and Desorption of La(III) on Pyrite. Desorbing Agent was $1x10^{-3}$ M $Ca(NO_3)_2$

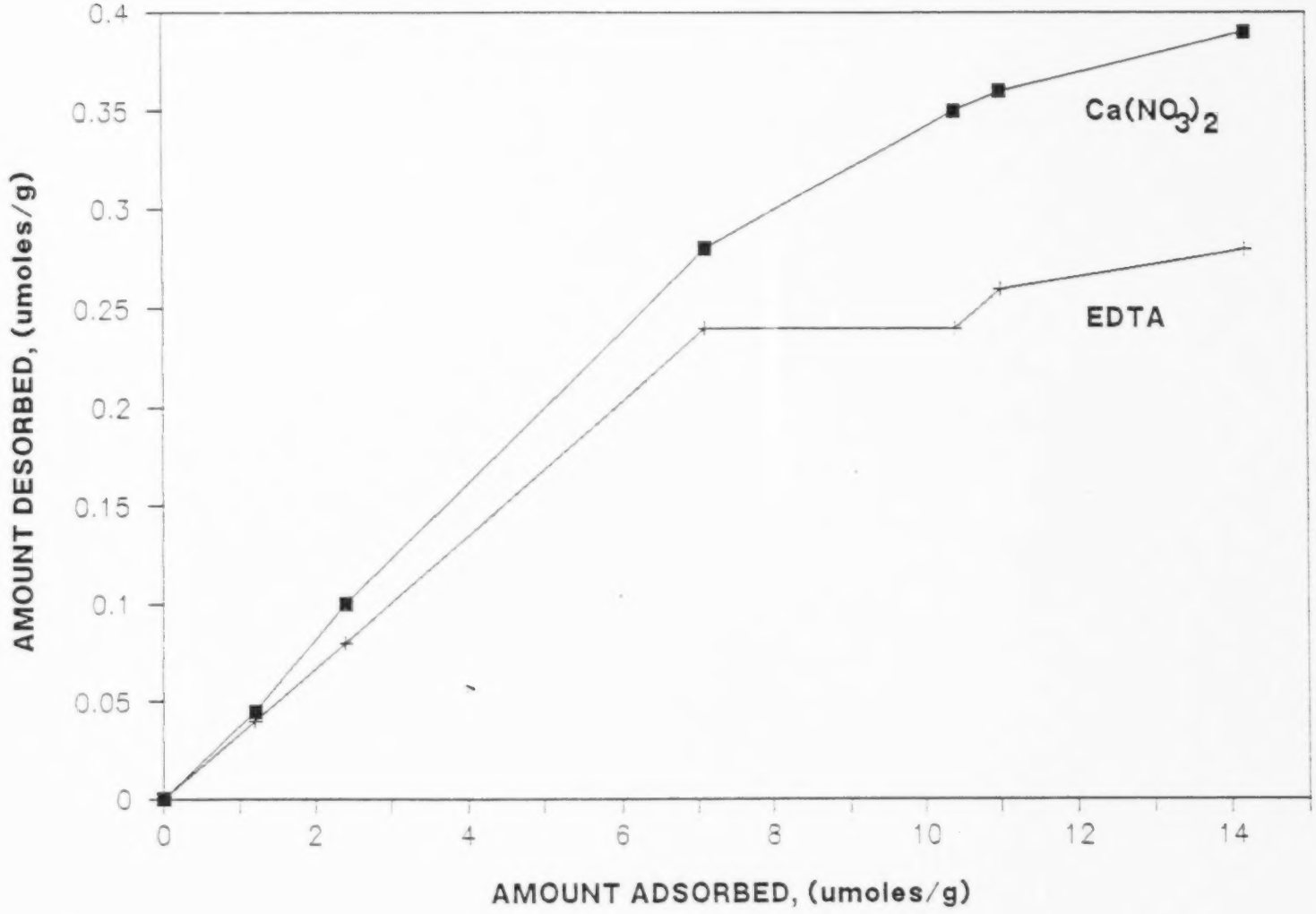

Figure 12. The Effect of Desorbing Agent on the Release of La(III) from Pyrite at pH=4.0

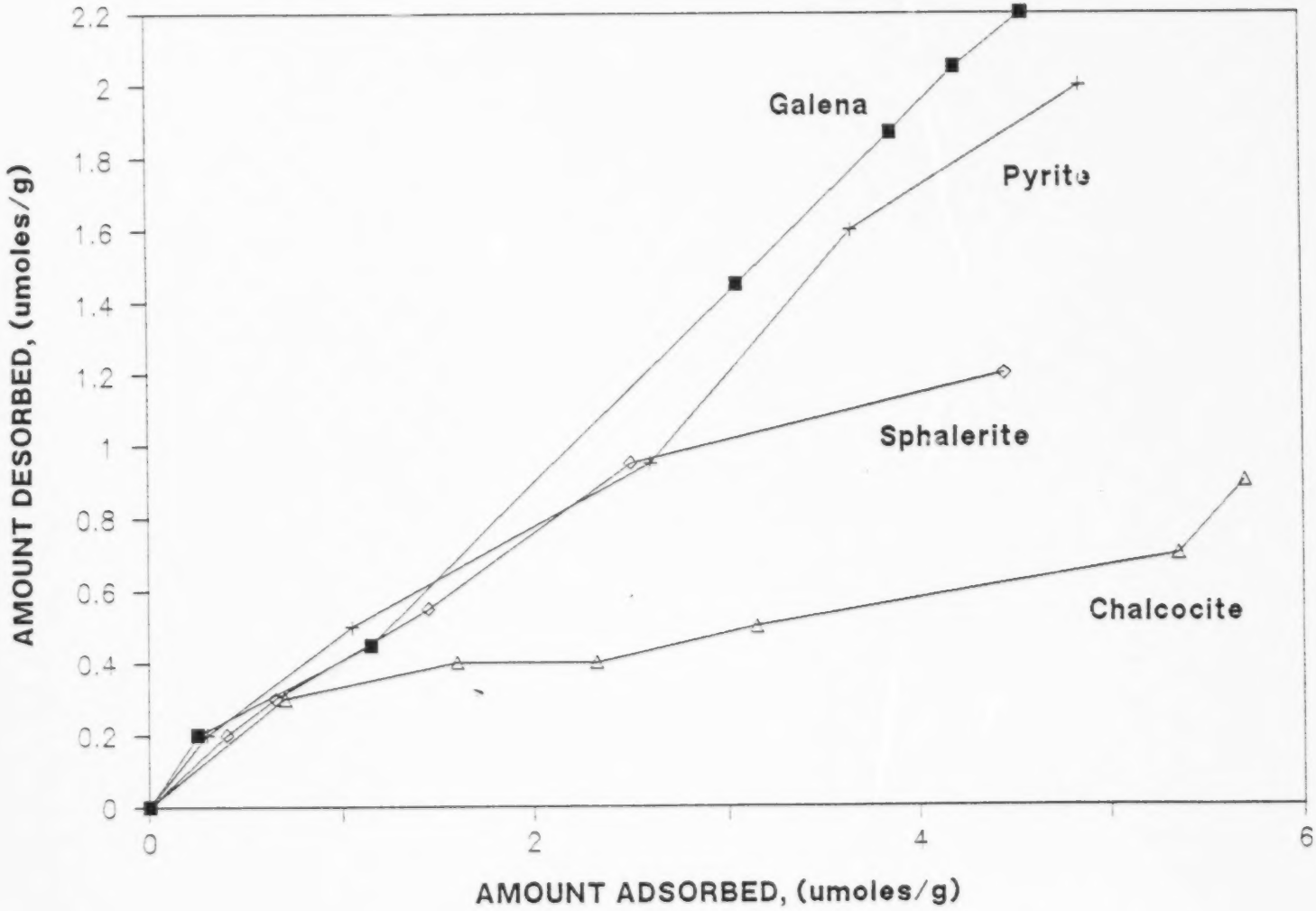

Figure 13. The Desorption of La(III) from Four Sulfide Minerals in the Absence of EDTA. Desorbing Agent Was 1.0×10^{-3} M $Ca(NO_3)_2$

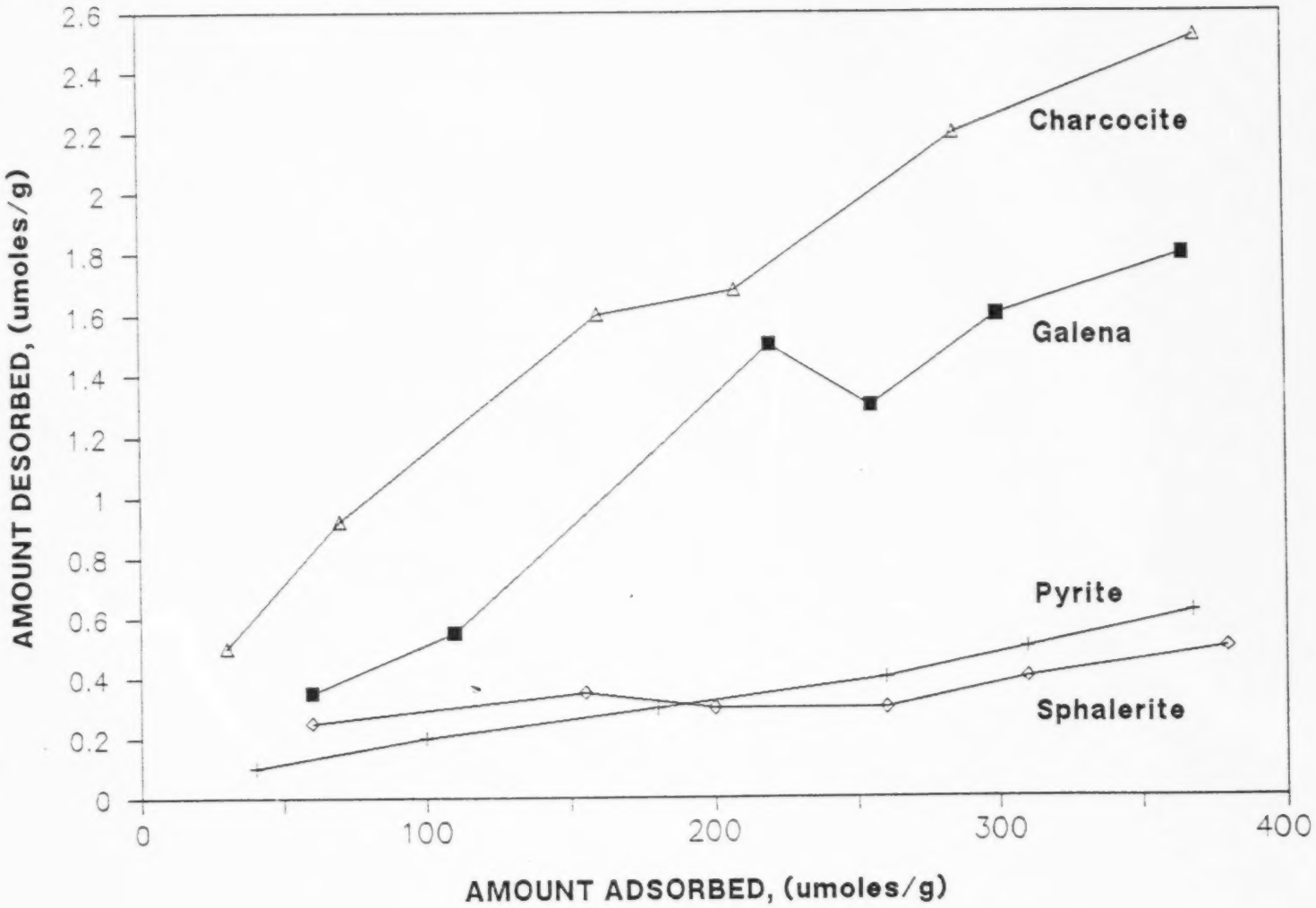

Figure 14. Desorption of La(III) - EDTA Complexes from Four Sulfide Minerals by $1x10^{-3}$ M $Ca(NO_3)_2$ at pH=4.0

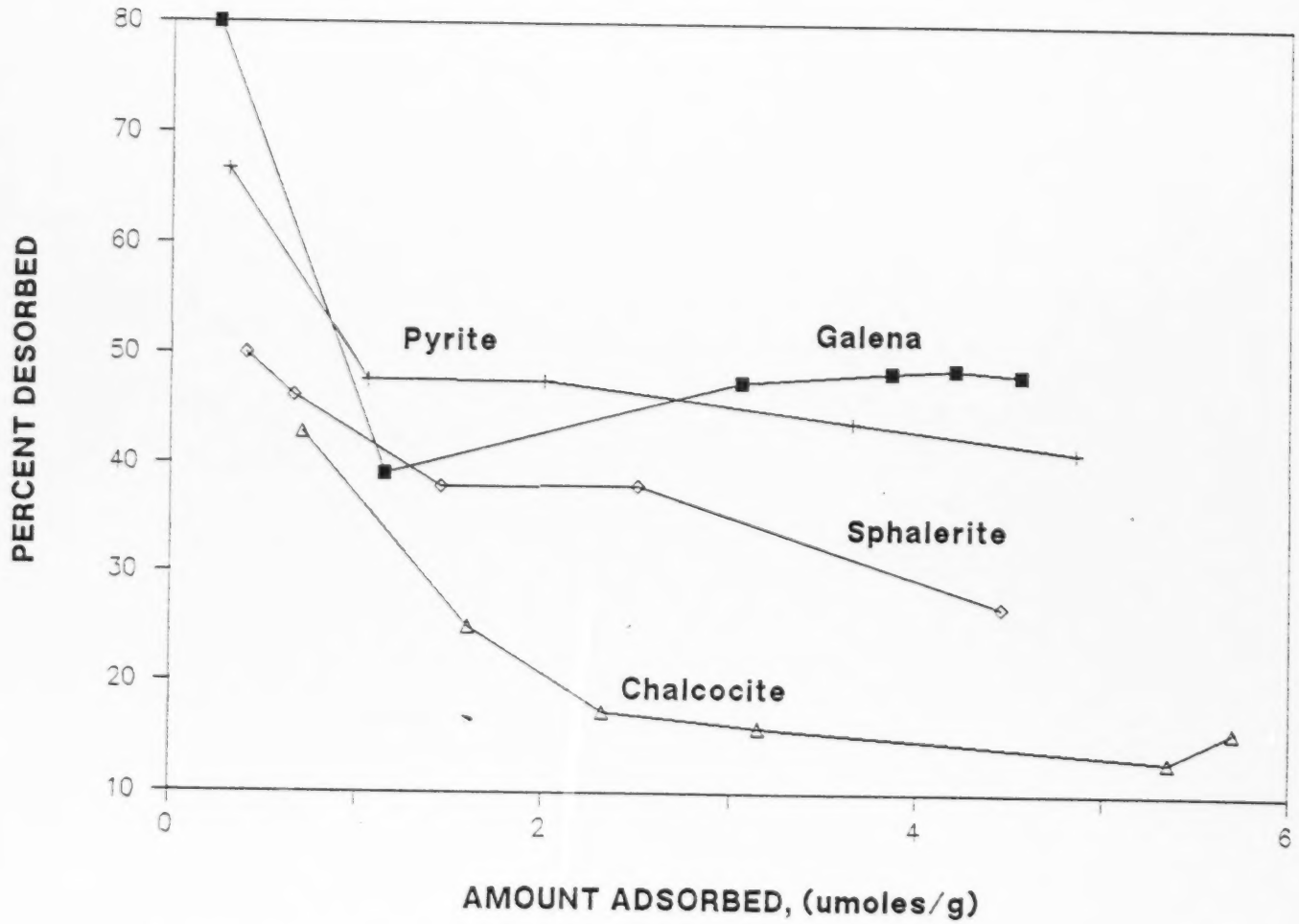

Figure 15. The Percent Desorption of La(III) from Four Sulfide Minerals in the Absence of EDTA. Desorbing agent was 1.0×10^{-3} M $Ca(NO_3)_2$

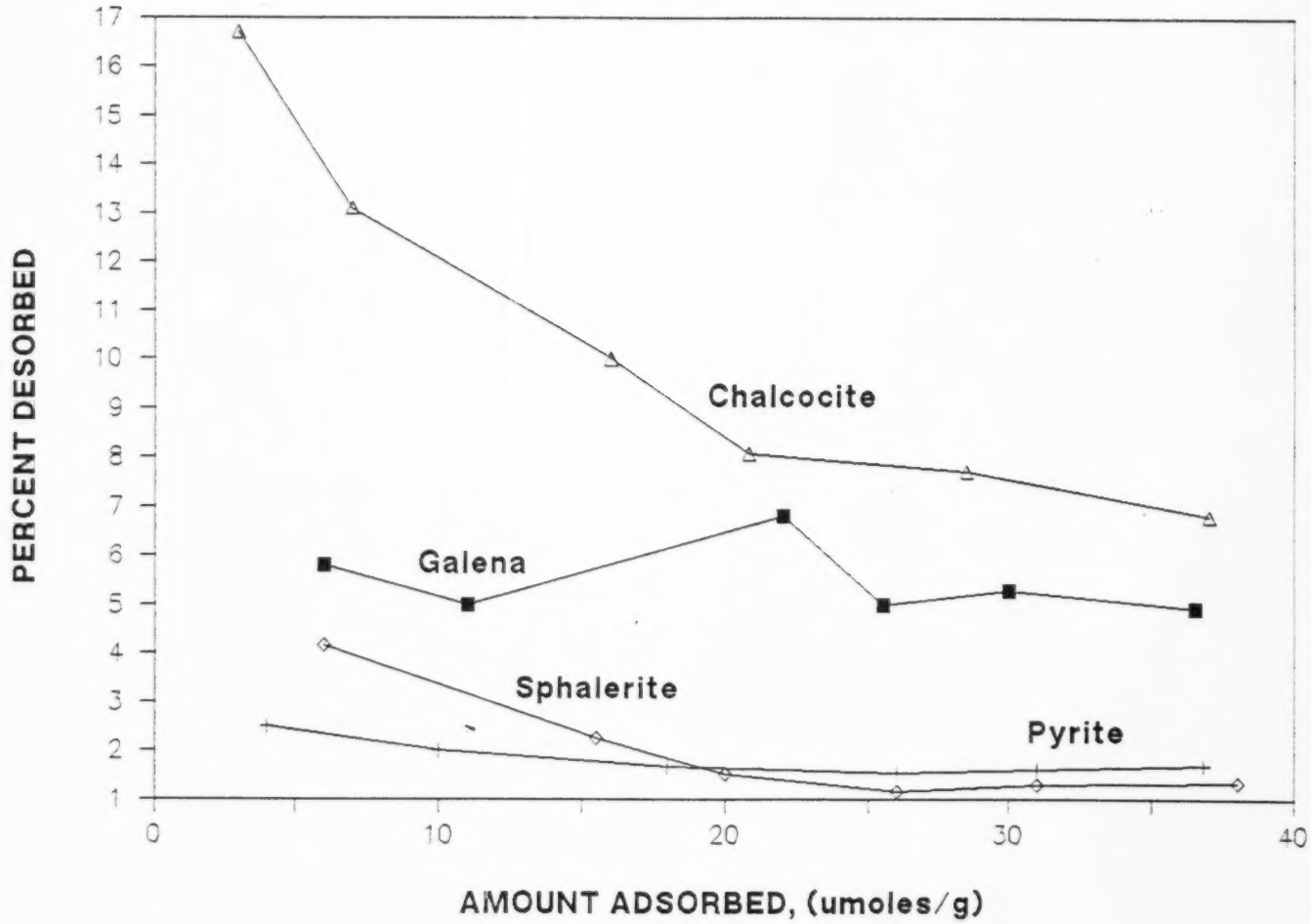

Figure 16. The Percent Desorption of La(III) - EDTA Complexes from Four Sulfide Minerals after Extraction with $1x10^{-3}$ M $Ca(NO_3)_2$